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**WO 01/48837 A2**

(54) Title: METHOD FOR MAKING HYDROGEN STORAGE ALLOY

(57) Abstract: A method for making a hydrided hydrogen storage alloy powder from component material. In the present method a material is worked at the same time it is hydrided. Working preferably involves comminution of the material.

## METHOD FOR MAKING HYDROGEN STORAGE ALLOY

### FIELD OF THE INVENTION

5 The instant invention relates generally to hydrogen storage alloys. More particularly, the invention relates to a new method for making hydrogen storage alloy materials.

### BACKGROUND OF THE INVENTION

10 Disclosed herein are hydrogen storage materials having high capacity and fast kinetics. In particular, at least a portion of the disclosure relates to modified Mg based hydrogen storage alloys and, specifically, to Mg based alloys having both hydrogen storage capacities higher than about 6 wt. % and extraordinary kinetics. Also disclosed are ways of making these materials.

15 These materials are made possible via application of the principles of disorder pioneered by Stanford R. Ovshinsky. These principles allow for tailoring of the material by controlling the particle and grain size, topology, surface states, catalytic activity, microstructure, and total interactive environments for storage capacity.

20 As the world's population expands and its economy increases, the atmospheric concentrations of carbon dioxide are warming the earth causing climate change. However, the global energy system is moving steadily away from the carbon-rich fuels whose combustion produces the harmful gas. Experts say atmospheric levels of carbon dioxide may be double that of the pre-industrial era by the end of the next century, but they also say the levels would be much  
25 higher except for a trend toward lower-carbon fuels that has been going on for more than 100 years. Furthermore, fossil fuels cause pollution and are a causative factor in the strategic military struggles between nations.

30 For nearly a century and a half, fuels with high amounts of carbon have progressively been replaced by those containing less. First wood, which is high in carbon, was eclipsed in the late 19<sup>th</sup> century by coal, which contains less carbon. Then oil, with a lower carbon content still, dethroned "King Coal" in the 1960's. Now analysts say that natural gas, lighter still in carbon, may be entering its heyday, and that the day of hydrogen – providing a fuel with no

carbon at all – may at last be about to dawn. As a result, experts estimate the world's economy today burns less than two-thirds as much carbon per unit of energy produced as it did in 1860.

In the United States, it is estimated, that the trend toward lower-carbon fuels combined with greater energy efficiency has, since 1950, reduced by about half the amount of carbon spewed out for each unit of economic production. Thus, the decarbonization of the energy system is the single most important fact to emerge from the last 20 years of analysis of the system. It had been predicted that this evolution will produce a carbon-free energy system by the end of the 21<sup>st</sup> century. In the near term, hydrogen will be used in fuel cells for cars, trucks and industrial plants, just as it already provides power for orbiting spacecraft. But ultimately, hydrogen will also provide a general carbon-free fuel to cover all fuel needs.

As noted in recent newspaper articles, large industries, especially in America, have long been suspicious of claims that the globe is warming and have vociferously negated the science of climate change. Electric utilities have even tried to stoke fears among ordinary folk that international treaties on climate change would cut economic growth and cost jobs. Therefore, it is very encouraging that some of the world's biggest companies, such as Royal Dutch/Shell and BP Amoco, two large European oil firms, now state plainly what was once considered heresy: global warming is real and merits immediate action. A number of American utilities vow to find ways to reduce the harm done to the atmosphere by their power plants. DuPont, the world's biggest chemicals firm, even declared that it would voluntarily reduce its emissions of greenhouse gases to 35% of their level in 1990 within a decade. The automotive industry, which is a substantial contributor to emissions of greenhouse gases and other pollutants (despite its vehicular specific reductions in emissions), has now realized that change is necessary as evidenced by their electric and hybrid vehicles. In this field, the assignee of the subject invention, has developed the Ovonic nickel metal hydride battery to make electric and hybrid vehicles possible.

Figure 1, taken from reliable industrial sources, is a graph demonstrating

society's move toward a carbon-free environment as a function of time starting with the use of wood in the early 1800s and ending in about 2010 with the beginning of a "hydrogen" economy. In the 1800s, fuel was primarily wood in which the ratio of hydrogen to carbon was about 0.1. As society switched to the use of coal and oil, the ratio of hydrogen to carbon increased first to 1.3 and then to 2. Currently, society is inching closer to the use of methane in which the hydrogen to carbon ratio is further increased to 4. However, the ultimate goal for society is to employ a carbon-free fuel, i.e., the most ubiquitous of elements, pure hydrogen. The obstacle has been the lack of solid state storage capacity and infrastructure. The inventor of the subject patent application has made this possible by inventing a 7% storage material (further improvements are very likely via additional research efforts) with exceptional absorption/desorption kinetics, that allow for the first time, a safe, high capacity means of storing, transporting and delivering pure hydrogen.

Hydrogen is the "ultimate fuel." In fact, it is considered by most to be "THE" fuel for the next millennium, and, it is inexhaustible. Hydrogen is the most plentiful element in the universe (over 95%) and was the first element created by the "Big-Bang." Hydrogen can provide an inexhaustible, clean source of energy for our planet which can be produced by various processes which split water into hydrogen and oxygen. The hydrogen can be stored and transported in solid state form. The instant patent application makes it possible to create a complete generation/storage/transportation/delivery system for such a hydrogen based economy. For example, economical, lightweight, triple-junction amorphous silicon solar cells (an invention pioneered by Stanford R. Ovshinsky) such as those set forth in U.S. Patent No. 4,678,679, (the disclosure of which is herein incorporated by reference) can be readily disposed adjacent a body of water, where their inherently high open circuit voltage can be used to dissociate water into its constituent gases, and collect the hydrogen so produced. Also, by placing these high efficiency solar panels on nearby farms, in water, or on land. Electricity can be generated to transport and pump the hydrogen into metal hydride storage beds that include the inventive metal hydride alloys disclosed

herein. The ultra-high capacities of these alloys allow this hydrogen to be stored in solid form for transport by barge, tanker, train or truck in safe, economical form for ultimate use. Energy is the basic necessity of life and civilization for any society today and the use of hydrogen in the manner described herein as the basic source of energy would end wars fought for control of fossil fuels. Instead of "from well to wheel," the phrase now recited will be "from source to wheel."

In the past considerable attention has been given to the use of hydrogen as a fuel or fuel supplement. While the world's oil reserves are depletable, the supply of hydrogen remains virtually unlimited. Hydrogen can be produced from coal, natural gas and other hydrocarbons, or formed by the electrolysis of water, preferably via energy from the sun which is composed mainly of hydrogen and can itself be thought of as a giant hydrogen "furnace". Moreover hydrogen can be produced without the use of fossil fuels, such as by the electrolysis of water using nuclear or solar energy, or any other form of economical energy (e.g. wind, waves, geothermal, etc.). Furthermore, hydrogen, although presently more expensive than petroleum, is an inherently low cost fuel. Hydrogen has the highest density of energy per unit weight of any chemical fuel and is essentially non-polluting since the main by-product of "burning" hydrogen is water. Thus, hydrogen can be a means of solving many of the world's energy related problems, such as climate change, pollution, strategic dependancy on oil, etc., as well as providing a means of helping developing nations.

While hydrogen has wide potential application as a fuel, a major drawback in its utilization, especially in mobile uses such as the powering of vehicles, has been the lack of an acceptable lightweight hydrogen storage medium. Storage of hydrogen as a compressed gas involves the use of large and heavy vessels. In a steel vessel or tank of common design only about 1% of the total weight is comprised of hydrogen gas when it is stored in the tank at a typical pressure of 136 atmospheres. In order to obtain equivalent amounts of energy as compared with gasoline, a container of hydrogen gas weighs about thirty times the weight of a container of gasoline. Additionally, large and very expensive compressors are required to store hydrogen as a compressed gas.

Hydrogen also can be stored as a liquid. Storage as a liquid, however,

presents a serious safety problem when used as a fuel for motor vehicles since hydrogen is extremely flammable. Liquid hydrogen also must be kept extremely cold, below  $-253^{\circ}\text{C}$ , and is highly volatile if spilled. Moreover, liquid hydrogen is expensive to produce and the energy necessary for the liquefaction process is a major fraction of the energy that can be generated by burning the hydrogen. Another drawback to storage as a liquid is the costly losses of hydrogen due to evaporation, which can be as high as 5% per day.

Storage of hydrogen as a solid hydride can provide a greater percent weight storage than storage as a compressed gas or a liquid in pressure tanks. Also, hydrogen storage in a solid hydride is safe and does not present any of the safety problems that hydrogen stored in containers as a gas or a liquid do because hydrogen, when stored in a solid hydride form, exists in its lowest free energy state. A desirable hydrogen storage material must have a high storage capacity relative to the weight of the material, a suitable desorption temperature, good kinetics, good reversibility, resistance to poisoning by contaminants including those present in the hydrogen gas and be of a relatively low cost. If the material fails to possess any one of these characteristics it will not be acceptable for wide scale commercial utilization.

A high hydrogen storage capacity per unit weight of material is an important consideration in applications where the hydride does not remain stationary. A low hydrogen storage capacity relative to the weight of the material reduces the mileage and hence the range of the vehicle making the use of such materials impractical. A low desorption temperature (in the neighborhood of  $300^{\circ}\text{C}$ ) is desirable to reduce the amount of energy required to release the hydrogen. Furthermore, a relatively low desorption temperature to release the stored hydrogen is necessary for efficient utilization of the available exhaust heat from vehicles, machinery, or other similar equipment.

Good reversibility is needed to enable the hydrogen storage material to be capable of repeated absorption-desorption cycles without significant loss of its hydrogen storage capabilities. Good kinetics are necessary to enable hydrogen to be absorbed or desorbed in a relatively short period of time. Resistance to poisons to which the material may be subjected during manufacturing and

utilization is required to prevent a degradation of acceptable performance.

The prior art metallic host hydrogen storage materials include magnesium, magnesium nickel, vanadium, iron-titanium, lanthanum pentanickel and alloys of these metals others. No prior art material, however, has solved the  
5      aforementioned problem which would make it suitable for a storage medium with  
widespread commercial utilization which can revolutionize the propulsion  
industry and make hydrogen a ubiquitous fuel.

Thus, while many metal hydride systems have been proposed, the Mg  
systems have been heavily studied since Mg can store over 7 weight % of  
10      hydrogen. While magnesium can store large amounts of hydrogen, its primary  
disadvantage is extremely slow kinetics. For example, magnesium hydride is  
theoretically capable of storing hydrogen at approximately 7.6% by weight  
computed using the formula:  $\text{percent storage} = H/H+M$ , where H is the weight of  
the hydrogen stored and M is the weight of the material to store the hydrogen (all  
15      storage percentages hereinafter referred to are computed based on this  
formula). Unfortunately, despite high storage capacity, prior art materials were  
useless because discharge of the hydrogen took days. While a 7.6% storage  
capacity is ideally suited for on board hydrogen storage for use in powering  
vehicles, it requires the instant invention to form Mg-based alloys operating on  
20      principles of disorder to alter previously unuseable materials and make them  
commercially acceptable for widespread use.

Magnesium is very difficult to activate. For example, U.S. Pat. No.  
3,479,165 discloses that it is necessary to activate magnesium to eliminate  
surface barriers at temperatures of 400 °C. to 425 °C. and 1000 psi for several  
25      days to obtain a reasonable (90%) conversion to the hydride state. Furthermore,  
desorption of such hydrides typically requires heating to relatively high  
temperatures before hydrogen desorption begins. The aforementioned patent  
states that the  $\text{MgH}_2$  material must be heated to a temperature of 277 °C. before  
desorption initiates, and significantly higher temperatures and times are required  
30      to reach an acceptable operating output. Even then, the kinetics of pure Mg are  
unacceptable, i.e., unuseable. The high desorption temperature makes the prior  
art magnesium hydride unsuitable.

Mg-based alloys have been considered for hydrogen storage also. The two main Mg alloy crystal structures investigated have been the  $A_2B$  and  $AB_2$  alloy systems. In the  $A_2B$  system,  $Mg_2Ni$  alloys have been heavily studied because of their moderate hydrogen storage capacity, and lower heat of formation ( $\sim 64$  kJ/mol) than Mg. However, because  $Mg_2Ni$  has the possibility of a storage capacity of up to 3.6 wt.% hydrogen, researchers have attempted to improve the hydrogenation properties of these alloys through mechanical alloying, mechanical grinding and elemental substitutions. However, 3.6 wt. % is not nearly high enough and the kinetics are likewise insufficient.

More recently, investigators have attempted to form  $MgNi_2$  type alloys for use in hydrogen storage. See Tsushio et al, Hydrogenation Properties of Mg-based Laves Phase Alloys, Journal of Alloys and Compounds, 269 (1998), 219-223. Tsushi et al. determined that no hydrides of these alloys have been reported, and they did not succeed in modifying  $MgNi_2$  alloys to form hydrogen storage materials.

Finally, we have worked on high Mg content alloys or elementally modified Mg. For instance, in U.S. Patent Nos. 5,976,276 and 5,916,381, Sapru, et al have produced mechanically alloyed Mg-Ni-Mo and Mg-Fe-Ti materials containing about 75 to 95 atomic percent Mg, for thermal storage of hydrogen. These alloys are formed by mixing the elemental ingredients in the proper proportions in a ball mill or attritor and mechanically alloying the materials for a number of hours to provide the mechanical alloy. While these alloys have improved storage capacities as compared with  $Mg_2Ni$  alloys, they have low plateau pressures.

Another example of modified high Mg content alloy is disclosed in U.S. Patent No. 4,431,561 ('561) to Ovshinsky et al., the disclosure of which is hereby incorporated by reference. In the '561 patent, thin films of high Mg content hydrogen storage alloys were produced by sputtering. While this work was remarkable in applying fundamental principles to drastically improve the storage capacities, it was not until the invention described herein that all necessary properties of high storage capacity, good kinetics and good cycle life were brought together.



In U.S. Pat. No. 4,623,597 ("the '597 patent"), the contents of which are incorporated by reference, Ovshinsky, described disordered multicomponent hydrogen storage materials for use as negative electrodes in electrochemical cells for the first time. In this patent, Ovshinsky describes how disordered materials can be tailor made to greatly increase hydrogen storage and reversibility characteristics. Such disordered materials are formed of one or more of amorphous, microcrystalline, intermediate range order, or polycrystalline (lacking long range compositional order) wherein the polycrystalline material may include one or more of topological, compositional, translational, and positional modification and disorder, which can be designed into the material. The framework of active materials of these disordered materials consist of a host matrix of one or more elements and modifiers incorporated into this host matrix. The modifiers enhance the disorder of the resulting materials and thus create a greater number and spectrum of catalytically active sites and hydrogen storage sites.

The disordered electrode materials of the '597 patent were formed from lightweight, low cost elements by any number of techniques, which assured formation of primarily non-equilibrium metastable phases resulting in the high energy and power densities and low cost. The resulting low cost, high energy density disordered material allowed such Ovonic batteries to be utilized most advantageously as secondary batteries, but also as primary batteries and are used today worldwide under license from the assignee of the subject invention.

Tailoring of the local structural and chemical order of the materials of the '597 patent was of great importance to achieve the desired characteristics. The improved characteristics of the anodes of the '597 patent were accomplished by manipulating the local chemical order and hence the local structural order by the incorporation of selected modifier elements into a host matrix to create a desired disordered material. The disordered material had the desired electronic configurations which resulted in a large number of active sites. The nature and number of storage sites was designed independently from the catalytically active sites.

Multiorbital modifiers, for example transition elements, provided a greatly

increased number of storage sites due to various bonding configurations available, thus resulting in an increase in energy density. The technique of modification especially provides non-equilibrium materials having varying degrees of disorder provided unique bonding configurations, orbital overlap and hence a spectrum of bonding sites. Due to the different degrees of orbital overlap and the disordered structure, an insignificant amount of structural rearrangement occurs during charge/discharge cycles or rest periods therebetween resulting in long cycle and shelf life.

The improved battery of the '597 patent included electrode materials having tailor-made local chemical environments which were designed to yield high electrochemical charging and discharging efficiency and high electrical charge output. The manipulation of the local chemical environment of the materials was made possible by utilization of a host matrix which could, in accordance with the '597 patent, be chemically modified with other elements to create a greatly increased density of catalytically active sites for hydrogen dissociation and also of hydrogen storage sites.

The disordered materials of the '597 patent were designed to have unusual electronic configurations, which resulted from the varying 3-dimensional interactions of constituent atoms and their various orbitals. The disorder came from compositional, positional and translational relationships of atoms. Selected elements were utilized to further modify the disorder by their interaction with these orbitals so as to create the desired local chemical environments.

The internal topology that was generated by these configurations also allowed for selective diffusion of atoms and ions. The invention that was described in the '597 patent made these materials ideal for the specified use since one could independently control the type and number of catalytically active and storage sites. All of the aforementioned properties made not only an important quantitative difference, but qualitatively changed the materials so that unique new materials ensued.

The disorder described in the '597 patent can be of an atomic nature in the form of compositional or configurational disorder provided throughout the bulk of the material or in numerous regions of the material. The disorder also

can be introduced into the host matrix by creating microscopic phases within the material which mimic the compositional or configurational disorder at the atomic level by virtue of the relationship of one phase to another. For example, disordered materials can be created by introducing microscopic regions of a different kind or kinds of crystalline phases, or by introducing regions of an amorphous phase or phases, or by introducing regions of an amorphous phase or phases in addition to regions of a crystalline phase or phases. The interfaces between these various phases can provide surfaces which are rich in local chemical environments which provide numerous desirable sites for electrochemical hydrogen storage.

These same principles can be applied within a single structural phase. For example, compositional disorder is introduced into the material which can radically alter the material in a planned manner to achieve important improved and unique results, using the Ovshinsky principles of disorder on an atomic or microscopic scale.

One advantage of the disordered materials of the '597 patent were their resistance to poisoning. Another advantage was their ability to be modified in a substantially continuous range of varying percentages of modifier elements. This ability allows the host matrix to be manipulated by modifiers to tailor-make or engineer hydrogen storage materials with all the desirable characteristics, i.e., high charging/discharging efficiency, high degree of reversibility, high electrical efficiency, long cycle life, high density energy storage, no poisoning and minimal structural change.

The differences between chemical and thermal hydrides are fundamental. The thermal hydride alloys of the present inventions have been designed as a distinct class of materials with their own basic problems to be solved, which problems as shown in the following Table 1 are antithetical to those to be solved for electrochemical systems.

These same attributes have not, until now, been achieved for thermal hydrogen storage alloys. Therefore, there has been a strong felt need in the art for high capacity, low cost, light weight thermal hydrogen storage alloy materials having exceptionally fast kinetics.

Table 1

	<b>Electrochemical Hydrogen Storage Material</b>	<b>Gas Phase (Thermal) Hydrogen Storage Material</b>
Mechanism	H <sub>2</sub> O molecule splits	H <sub>2</sub> dissociates at the material surface
Environment	Alkaline oxidizing environment (KOH electrolyte)	H <sub>2</sub> gas – very susceptible to poisoning by oxygen (inoperative in presence of KOH)
Kinetics	Hydrogen storage/release at room temperature	Hydrogen storage anywhere from 20°C to 100°C
Thermodynamics	Specific range of useful M-H bond strength	M-H bond strength of any degree is acceptable
Thermal Conductivity	Small effect	Large effect
Electrical Conductivity	Large effect	Small effect
Chemical Reaction	$M + H_2O + e^- \rightleftharpoons MH + OH^-$	$H_2(g) \rightleftharpoons 2H$

### SUMMARY OF THE INVENTION

An object of the present invention is to provide a more efficient and cost effective method of forming a hydrided hydrogen storage material. This object is satisfied by a method for making a hydrogen storage material, said method comprising the steps of: providing a solid hydrogen storage alloy; and working said solid material in a hydrogen atmosphere at conditions sufficient to hydride said solid material.

Preferably, the providing step comprises the steps of: providing component materials; melting said component materials together to form a molten alloy; rapidly solidifying said molten alloy to form said solid alloy.

### BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a graph having time plotted on the abscissa and the H/C ratio plotted on the ordinate, said graph demonstrating the movement of society toward carbon-free sources of fuel;

Figure 2 is a graphical, stylistic depiction of the characteristics required by hydrogen storage alloys in order for such alloys to have the required kinetic properties required to propel fuel cell and internal combustion engines;

Figure 3 is a graph of the Pressure Composition Temperature (PCT) curves of alloy FC-10 at 3 different temperatures;

Figure 4 is a graph of the PCT curves of alloy FC-76 at 3 different temperatures;

Figure 5 is a plot of the absorption kinetics of the FC-76 alloy, specifically plotted is weight % hydrogen absorption versus time for 3 different temperatures;

Figure 6 is a plot of the desorption kinetics of the FC-76 alloy specifically plotted is weight % hydrogen desorption versus time for 3 different temperatures;

Figure 7 is a plot of the absorption kinetics of the FC-86 alloy specifically plotted is weight % hydrogen desorption versus time for 3 different temperatures;

Figure 8 is a plot of the absorption kinetics of FC-76 alloy powders having two different particle sizes;

Figure 9 shows an embodiment of the instant invention where a support means bonded with the hydrogen storage alloy material is spirally wound into a coil;

Figure 10 shows an alternate embodiment of the instant invention where a support means bonded with the hydrogen storage alloy material is assembled as a plurality of stacked disks;

Figure 11, shows a schematic representation of a hydrogen gas supply system which utilizes the alloy of the instant invention for powering an internal combustion engine vehicle; and

Figure 12, shows a schematic representation of a hydrogen gas supply system which utilizes the alloy of the instant invention for powering for a fuel cell vehicle.

## DETAILED DESCRIPTION OF THE INVENTION

Mg stores large amounts of hydrogen. However, the kinetics of hydrogen storage in pure Mg are less than desirable. That is, while pure Mg can store

upwards of 7.6 wt. % hydrogen, the Mg-H bond is very strong (75 kJ/mol) making release of the stored hydrogen difficult and therefore pure Mg is not a commercially viable hydrogen storage material. Thus, Mg alone is not sufficient, but utilizing the principle of disorder and local order, compositional (chemically induced) and structural disorder (rapid quench) can be used to create a different distribution of elements. This breakthrough has been made possible by examining the materials as a system and by utilizing chemical modifiers and the principles of disorder and local order, pioneered by Stanford R. Ovshinsky, in such a way as to provide the necessary local order environments for storage. These principles allow for tailoring of the material by controlling the particle size, topology, surface states, catalytic ability (including catalytic sites and surface area), microstructure, nucleation and growth rate of crystallites both on the surface and in the bulk, and storage capacity both structural and interstitial. Figure 2 is a graphical, stylistic depiction of the characteristics required by hydrogen storage alloys in order for such alloys to have the required kinetic properties required to propel fuel cell and internal combustion engines and schematically illustrates these concepts.

Specifically, small particles have unique properties that bridge the gap between crystalline and amorphous solids, i.e. small geometry gives rise to new physics. It is to be noted that 50 Angstrom particles are "mostly surface," thereby giving rise to new topologies and unusual bonding configurations. Also, 21% of all atoms in a 50 Angstrom particle are on the surface and another 40% are within one atom of the surface. Thus compositional disorder in multi-element micro-alloys is large in small particles, e.g. in a 50 Angstrom particle, each element in a 10 element alloy will show 3% variation in concentration just due to statistics. With such small particles, quantum confinement effects are apparent and band structure effects are disturbed.

By applying the principles of atomic engineering and tailoring of the local environment, magnesium can be modified to store more than 6 wt.% hydrogen, with significantly increased kinetics which allows for economic recovery of the stored hydrogen. The increased kinetics allows for the release of hydrogen at lower temperatures, thus increasing the utility of metal hydride storage in

hydrogen based energy systems. Thus the instant alloys provide commercially viable, low cost, low weight hydrogen storage materials.

In general the alloys contain greater than about 90 weight % magnesium, and contain at least one modifier element. The at least one modifier element  
5 creates a magnesium based alloy which is capable of storing at least 6 weight % hydrogen and which is capable of absorbing at least 80% of the full storage capacity of hydrogen in under 5 minutes at 300 °C. More preferably the modified alloy stores at least 6.5 weight % hydrogen and is capable of absorbing 80% of the full storage capacity of hydrogen in under 2 minutes at 300 °C. Most  
10 preferably the modified alloy stores at least 6.9 weight % hydrogen and is capable of absorbing 80% of the full storage capacity of hydrogen in under 1.5 minutes at 300 °C. The modifier elements mainly include Ni and Mm (misch metal) and can also include additional elements such as Al, Y and Si. Thus the alloys will typically contain 0.5-2.5 weight % nickel and about 1.0-4.0 weight %  
15 Mm (predominantly contains Ce and La and Pr). The alloy may also contain one or more of 3-7 weight % Al, 0.1-1.5 weight % Y and 0.3-1.5 weight % silicon. A few examples will help to illustrate the instant invention.

#### EXAMPLE 1

20 A modified Mg alloy having the designation FC-10 was made which has the composition: 91.0 wt.% Mg, 0.9 wt.% Ni, 5.6 wt.% Al, 0.5 wt.% Y and 2.0 at% Mm. The individual raw alloying elements were mixed in a glove box. The mixture was placed in a graphite crucible and the crucible was placed in a furnace. The crucible had a 2.0 mm boron nitride orifice at the bottom thereof  
25 which is plugged by a removable boron nitride rod. The furnace was pumped down to very low pressure and purged three times with argon. The argon pressure within the furnace was brought up to 1 psi and kept at this pressure as the crucible was heated to 600 °C. Once the melt was ready, the boron nitride rod was lifted and argon was injected into the furnace under pressure. The  
30 molten alloy flowed out of the graphite crucible through the boron nitride orifice and onto a non-water-cooled, horizontally spinning, copper wheel. The wheel, which spins at about 1000 rpm, solidifies the molten alloy into particles which

then bounce off a water-cooled copper cap which covers the spinning wheel, and drop into a stainless steel pan where they gradually cool. Five grams of the solidified alloy flakes were mixed with 100 mg of graphite grinding aid. The mixture was mechanically ground for 3 hours. The ground alloy was then  
5 classified by sieving to recover material having a particle size of between 30 and 65 microns. This alloy has a storage capacity of about 6.5 wt.% hydrogen and absorbs 80 % of the maximum capacity in less than 5 minutes at a temperature of about 300 °C. Other details of the alloy properties are presented below.

## 10 EXAMPLE 2

A modified Mg alloy having the designation FC-76 was made which has a composition: 95.6 wt.% Mg, 1.6 wt.% Ni, 0.8 wt.% Si and 2.0 wt% Mn. The alloy was formed in the same manner as Example 1, however, the furnace  
15 temperature was 850 °C and the orifice size was 2.5 mm. This alloy has a storage capacity of about 6.9 wt.% hydrogen and absorbs 80 % of the maximum capacity in less than 1.5 minutes at a temperature of about 300 °C. Other details of the alloy properties are presented below.

## EXAMPLE 3

20 A modified Mg alloy having the designation FC-86 was made which has a composition: 95 wt.% Mg, 2 wt.% Ni and 3.0 wt% Mn. The alloy was formed in the same manner as Example 1, however, the furnace temperature was 750 °C and the wheel speed was 1400 rpm. This alloy has a storage capacity of about 7 wt.% hydrogen and absorbs 80 % of the maximum capacity in less than 2.3  
25 minutes at a temperature of about 275 °C. Other details of the alloy properties are presented below.

The alloys of the instant invention are unique in their combination of high storage capacity and excellent absorption/desorption kinetics. The instant inventors have found that a combination of both alloy composition and particle  
30 size of the hydrogen storage material have a significant effect on the kinetics. That is, the instant inventors have found that the kinetics of the material (regardless of specific composition) improve with decreasing particle size.



Specifically, the instant inventors have found that materials having a particle size of between about 30 and 70 microns are the most useful. This particle size gives excellent kinetics while still being capable of being manufactured. Increasing particle size eases manufacturing, but drastically reduces the kinetics of the material, while decreasing particle size is nearly impossible because of the high ductility of these Mg based alloys. In fact, the use of gas atomization may be required in industry to manufacture bulk quantities of the particulate alloy specifically because the alloys are too ductile to be ground efficiently.

Figure 3 is a graph of the Pressure-Composition -Temperature (PCT) curves of alloy FC-10 at 279 °C (represented by the  $\circ$  symbol), 306 °C (represented by the  $\Delta$  symbol) and 335 °C (represented by the  $\_$  symbol). The graph shows that the alloy has plateau pressures of 1050 Torr at 279 °C, 2200 Torr at 306 °C and 4300 Torr at 335 °C. The PCT curve shows that the FC-10 alloy has a maximum capacity of about 6.5 weight % hydrogen, and a hydrogen bond energy of about 70 kJ/mole.

Figure 4 is a graph of the PCT curves of alloy FC-76 at 278 °C (represented by the  $\blacksquare$  symbol), 293 °C (represented by the  $\blacklozenge$  symbol) and 320 °C (represented by the  $\Delta$  symbol). The graph shows that the alloy has plateau pressures of 750 Torr at 278 °C, 1100 Torr at 293 °C and 2400 Torr at 320 °C. The PCT curve shows that the FC-76 alloy has a maximum capacity of about 6.9 weight % hydrogen, and a hydrogen bond energy of about 75 kJ/mole.

Figure 5 is a plot of the absorption kinetics of the FC-76 alloy. Specifically, weight % hydrogen absorption versus time is plotted for 3 temperatures 275 °C ( $\square$  symbol), 300 °C ( $\circ$  symbol), and 325 °C ( $\_$  symbol). As can be seen, at 275 °C the alloy absorbs 80 % of it's total capacity in 1.3 minutes, at 300 °C the alloy absorbs 80 % of it's total capacity in 1.4 minutes, and at 325 °C the alloy absorbs 80 % of it's total capacity in 2.0 minutes.

Figure 6 is a plot of the desorption kinetics of the FC-76 alloy. Specifically, weight % hydrogen desorption versus time is plotted for 3 temperatures 275 °C ( $\square$  symbol), 300 °C ( $\circ$  symbol), and 325 °C ( $\_$  symbol). As can be seen, at 275 °C the alloy desorbs 80 % of it's total capacity in 8.0

minutes, at 300 °C the alloy desorbs 80 % of it's total capacity in 3.4 minutes, and at 325 °C the alloy desorbs 80 % of it's total capacity in 2.5 minutes.

Figure 7 is a plot of the absorption kinetics of the FC-86 alloy.

Specifically, weight % hydrogen absorption versus time is plotted for 3  
5 temperatures 230 °C (  $\square$  symbol), 240 °C ( $\circ$  symbol), and 275 °C ( $\_$  symbol). As can be seen, at 230 °C the alloy absorbs 80 % of it's total capacity in 5.2 minutes, at 300 °C the alloy absorbs 80 % of it's total capacity in 2.4 minutes, and at 325 °C the alloy absorbs 80 % of it's total capacity in 2.3 minutes.

Figure 8 is a plot of the absorption kinetics of FC-76 alloy powders having  
10 two different particle sizes. Specifically, weight % hydrogen absorption versus time is plotted for material having a particle size range of 75-250 microns ( $\circ$  symbol), and 32-63 microns (  $\square$  symbol). As can be seen, the smaller particle size greatly enhances the absorption kinetics.

Also disclosed herein is an efficient and cost effective method for making  
15 a hydrided hydrogen storage material. Preferably, the material is either a substantially pure metal or an alloy. This method is applicable to the hydrogen storage materials described in the present application.

The first step in the method for making a hydrided hydrogen storage material is to form an appropriate "solid" hydrogen storage material. The solid  
20 hydrogen storage material may be in any solid form. For example, it may in the form of ingots, ribbons, powder, threads, etc.

The solid alloy may be formed in many different ways. Preferably, the solid alloy may be formed from either a rapid solidification process or from a mechanical alloying process. More preferably, the solid alloy is formed from a  
25 rapid solidification process. There are many different ways in which rapid solidification may be accomplished. Preferably, rapid solidification may be accomplished by melt spinning, jet casting, multiple jet casting, planar flow casting, gas atomization, ultrasonic atomization, centrifugal atomization are used. Any of these rapid solidification processes can be used regardless of the  
30 particular apparatus used or details of the process itself. More preferably rapid solidification may be accomplished by using melt spinning or by gas atomization. Most preferably, rapid solidification is accomplished by melt spinning.

To form the solid alloy by rapid solidification, the appropriate components materials are placed into a melt furnace where they are melted together to form a molten material. If the component materials are different metals, then the molten material is a molten alloy. The melt furnace is heated to a temperature sufficient to melt each of the component materials. The melt furnace both heats and mixes the starting materials so that they form a substantially homogenous molten material. Heating may be accomplished by resistive heating, inductive heating or any other technique which will not add impurities to the liquified and molten material. Preferably, heating is accomplished by inductive heating which uses radio frequency energy to melt the component materials. Mixing may be accomplished by an inductive mixer which uses the same radio frequency energy to agitate and stir the molten material to ensure that the alloy remains a homogeneous mixture.

After a sufficient quantity of the homogenous molten material is formed in the melt furnace, it is then cooled and solidified. This process is known as "casting". The casting process used to cool and solidify the molten material in the present invention is preferably that of "rapid solidification". Rapid solidification refers to methods and processes for rapidly quenching a material from the liquid state into the solid state at a quench rate sufficiently high to freeze the positions of the atoms into the atomic arrangement of the material before complete crystallization has occurred. Typically, the material is ejected in its liquified state into a high quench environment such as onto a chill wheel where it solidified before complete crystallization can begin. As discussed, the rapid solidification is preferably accomplished by melt spinning, jet casting, multiple jet casting, planar flow casting, gas atomization, ultrasonic atomization, centrifugal atomization are used. Any of these rapid solidification processes can be used regardless of the particular apparatus used or details of the process itself.

Rapid solidification of the instant metals or alloys may be achieved by melt spinning the molten alloy onto the peripheral surface of a rapidly rotating wheel called a "chill wheel". Typically, the chill wheel is formed from a thermally conductive material such as copper, aluminum or an alloy thereof. The chill

wheel, because of its mass and because of the significant difference in temperature between the molten alloy and the ambient temperature of the wheel, need not be cooled in order to provide a cold moving substrate relative to the molten alloy. Alternately, the chill wheel may include means for additional cooling such as a circulating cooling liquid through its interior.

In one embodiment, the molten material flows from the melt furnace and into a casting crucible. Like the melt furnace, the casting crucible may include both a heater and a mixer. Preferably the heater is an inductive heater and the mixer is an inductive mixer. The casting crucible has an orifice serving as an exit path for the molten material. One embodiment of the invention employs a casting crucible made from a boron nitride alloy. In one embodiment, the crucible is preferably heated to a temperature between about 1000°C to a temperature of about 2100°C.

The chill wheel is preferably positioned below the casting crucible orifice. The weight of the molten material within the crucible pushes the molten material through the crucible orifice and onto the surface of the rotating chill wheel whereupon it immediately solidifies into the solid hydrogen storage material and breaks apart into solid metal flakes called "ribbons".

The diameter of the crucible orifice as well as the level of molten material in the crucible affects the volumetric flow rate of the molten alloy out of the crucible and onto the surface of the chill wheel. In one embodiment, the crucible orifice preferably has a diameter between about 0.0635 cm to about 0.114 cm and is located about 1-2 mm above the chill wheel. The flow rate of the molten alloy as well as the rotational speed of the chill-wheel affect the width and thickness of the ribbons produced by the rapid solidification process. Generally, an increase in the surface velocity of the chill wheel results in a thinner ribbon while the reduction of the surface velocity results in a thicker ribbon.

Control of the volumetric flow rate of molten material from the crucible may be achieved by controlling the level of the molten material maintained in the crucible. Increasing the level of the molten material increases the pressure at the crucible orifice, thereby increasing the flow rate out of the crucible and onto

the chill wheel. Generally, the volumetric flow rate of molten alloy onto the chill wheel, the rotational speed of the chill wheel, and the temperature of the chill wheel all affect the quench rate of the molten material and thus the microstructure of the solid hydrogen storage material formed by the rapid solidification process. Hence, these parameters may be varied in order to achieve the desired structure of the solid material.

The rapid solidification process using a chill wheel may be carried out in a controlled atmosphere. The apparatus may use a plurality of gas jets to direct an inert gas, such as argon, onto the ribbon before it leaves the chill wheel. This allows control of the quench duration. Other means for aiding the solidification of the molten material may be used.

In one embodiment of the invention, a copper beryllium chill wheel is housed within an evacuated chamber that is continuously filled with argon. In one embodiment it is preferable that the temperature of the chill wheel is a temperature between about -273°C to about 90°C. The chill wheel itself preferably has a copper beryllium surface, although any high hardness, high melting point material may be used.

As discussed above, rapid solidification techniques other than melt spinning may be used to allow the formation of the microstructure necessary to create the solid hydrogen storage material of the instant invention having the requisite density of catalytic and hydrogen storage sites. In particular, gas atomization may be used to rapidly solidify the molten alloy. In this case, rather than forming ribbons, the molten material is solidified to form regularly or irregularly shaped particles. Still other techniques include planar flow casting, plasma spray, jet casting, multiple jet casting as well as other accelerated quenching processes may be substituted for melt spinning.

After cooling, the solid hydrogen storage material is formed. As discussed, the solid hydrogen storage alloy may have many different forms. For example, it may be in the form of ribbons If a melt spinning process is used to solidify the alloy. However, it may be in the form of a particulate or powder If a gas atomization technique was used to form the solid alloy. In general, it may be in any solid form including, but not limited to, ribbons, flakes, particulate, ingots,

threads, etc.

After the solid alloy is formed, it is then hydrided to form a hydrided hydrogen storage material. Hydriding embrittles the solid hydrogen storage alloy. The hydriding procedure includes contacting the material with a hydrogen gas under the appropriate temperature, pressure and time conditions to form the hydride of the material. The solid hydrogen absorbing alloy may be placed in a reaction vessel which is subsequently sealed and evacuated. Preferably, the pressure is less than about  $10^{-3}$  torr. More preferably, the pressure is less than about  $10^{-4}$  torr, and more preferably the pressure is less than about  $10^{-5}$  torr.

The vessel is subsequently pressurized with hydrogen gas. The pressure of the hydrogen gas may be between about 10 bar and about 100 bar. The actual operating conditions depend upon the composition of the material and its geometry. Materials having a slower diffusion rate or lower interstitial mobility for hydrogen will require more time for suitable embrittlement. The factors that affect the mobility of hydrogen through the phase regions and into the material's structure will determine the pressure, time and temperature necessary to form a hydride of the material and effectuate suitable embrittlement. The vessel may be cooled during the hydriding step to prevent any temperature increase. The temperature inside the vessel rises as the material is exposed to the hydrogen due to the exothermic nature of the hydride formation reaction. The hydriding reaction spontaneously starts upon exposure to hydrogen gas. Initial heating of the material may accelerate the hydriding step.

The effects of hydriding can be modelled by the ideal gas law. Sufficient embrittlement for easy size reduction of some materials does not require complete hydride formation. Using the ideal gas law and the amount of hydrogen absorbed for sufficient embrittlement, the reaction vessel necessary to embrittle a given batch of material can be calculated.

It was noted above that hydriding is an exothermic reaction. Hence, the metal hydride formed as a result of hydriding has a lower energy and is more stable than the state that surmounted the chemical, physical, electronic and catalytic barriers that have heretofore been considered insoluble. Consequently, the hydride of a metal or alloy is more stable and less flammable than the metal or

alloy. Hence, in addition to making the material more brittle and thus more suitable for mechanical grinding, the hydriding step also makes the materials more suitable for shipment and storage.

The present method for making a hydrided hydrogen storage material is unique in that the solid hydrogen storage material is "worked" at the same time that it is hydrided. Generally, "working" a material refers to applying an external force to the material. Examples of forces include tensile forces, compressive forces and shearing forces. The external forces may be due to external loads. Examples of loads include static loads which are applied slowly and remain nearly constant, dynamic loads which vary with time, and impact loads (i.e., from a striking object).

The external forces may be "mechanical" in nature. For example, they may be due to the transfer of kinetic energy from a moving foreign object (for example, the grinding balls of a grinding mill). However, the external forces may also be acoustical in nature such as from shock waves and explosions. It is also conceivable that the external forces be electromagnetic and/or thermal in nature.

It is noted that "working" includes cold working and hot working. Working may result in a plastic deformation of the material.

The working step may include comminution of the material. A material is worked when it is comminuted (reduced in size) by attriting, grinding, crushing, pulverizing, milling or the like. The attriting and/or grinding and/or milling may be performed in an attritor, ball mill, drum mill, ball mill, roller mill, airjet mill, vibratory mill, sand mill, or the like. An example of an attritor is provided in U.S. Patent No. 5,464,163, the disclosure of which is incorporated by reference herein. It is possible the comminution may also be performed by a device such as a jaw crusher, air-hammer, hardened mortar and pestle, etc. Typically, in a device such as an attritor, large rotating paddles are used to continuously stir a bed of steel balls. The moving steel balls provide sufficient shear force to continue to attrit or grind the solid material pieces so as to reduce the solid to a powder.

A material is also worked when it is forged or hammered. For example, a material may be hammered or struck by foreign objects as in an attritor, ball mill,

drum mill or the like. Repeatedly hammering a material may change its microstructure so as to mechanically alloy the material.

The working step may be effective to mechanically alloy the material with additional components. Mechanical alloying is a well known technique to alloy  
5 two or more metals together. In particular, the technique is useful for alloying two or more metal which typically are non-miscible in one another. While not wishing to be bound by theory, it is believed that mechanical alloying occurs due to repeated welding, fracturing and rewelding of the material particulate.

Generally, the materials that are mechanically alloyed together are violently  
10 agitated in an attritor, ball mill, drum mill or the like, by very hard freely moving bodies (i.e., steel or ceramic balls). Other methods for mechanical alloying of materials are described in U.S. Patent No. 5,074,908, the disclosure of which is incorporated by reference herein. It is noted that the mechanical alloying process may be used to change the microstructure of a material even without  
15 additional components.

A material may also be "worked" by modifying its surface. For example, the grinding process may be used to modify the surface of a material. For example, grinding may be used to coat the particles of one material with a surface coating of another material. Hence, by choosing the appropriate  
20 grinding conditions, the high speed grinding device (such as the attritor mill, ball mill, drum mill, roller mill, airjet mill, vibratory mill etc) may be used to provide for a mechanical surface modification/coating process. This allows a first material (element, compound, alloy, composite, etc) - i.e., the coating material, to be coated onto a second material (element, compound, alloy, composite, etc) - i.e.,  
25 the core material. In the process, the core material is deposited into the mechanical alloying chamber of the attritor. The core material may be pretreated while within the mechanical alloying chamber before the coating material is deposited into the chamber. The pretreatment may consist of mechanically alloying the core material, with or without additional materials being added (i.e.,  
30 grinding aids, alloying ingredients, etc). After any pretreatment has occurred, the coating material is then added to the alloying chamber of the attritor. This coating material may be in the form of smaller particles than the core material.



The two materials are now mechanically alloyed and the time, temperature, and speed of the high speed grinding mill is controlled such that the surface of the core material is alloyed with and coated by the coating material, while the central portion of the particles of the core material is not alloyed with the coating material.

Materials are also being "worked" when they are agglomerated together with other materials to form larger sized particles. Preferably, the appropriate starting materials may be placed in a grinding device and ground together. Preferably these materials have a high ductility.

Preferably, the working step is effective to comminute the solid hydrogen storage material. The comminution is preferably accomplished by an attriting, grinding, and/or milling process. The working step preferably comminutes the solid material so as to form a powder having the appropriate particle size. The desired particle size may be less than about 70 microns. Preferably, the desired particle size is less than about 50 microns. In one embodiment of the invention, the preferred particle size is between about 30 and about 70 microns.

In the present invention, the material is comminuted in a hydrogen atmosphere. Preferably, the hydrogen atmosphere has a pressure between about 10 bar and about 100 bar. More preferably, the hydrogen atmosphere has a pressure between about 20 bar and about 60 bar.

By attriting and/or grinding and/or milling the solid material in an atmosphere of hydrogen at the appropriate pressure and temperature, the solid alloy material is hydrided at the same time that it is comminuted to small particles. As the alloy particles are reduced in size, more of the alloy surface is exposed to the surrounding hydrogen atmosphere thereby further increasing hydrogen penetration into the alloy. The increased hydrogen penetration makes the alloy material more brittle, thereby allowing the grinding action of the high speed mill to further reduce the size of the alloy particles. Hence, comminuting and hydriding at the same time results in a synergistic effect which provides for a much more efficient, less time consuming and less expensive process for forming the hydrided hydrogen storage alloy powder (i.e., more efficient, less time consuming and less expensive than if the comminuting step and the

hydriding step were done inceptently). It is noted that the grinding process may be facilitated further by using a grinding agent, such as carbon, when grinding the alloy materials.

Hence, in general, by carefully selecting the appropriate conditions, a solid alloy (or other precursor materials) may be "worked" so that at least one or more of the following occurs: comminuting, hydriding, mechanically alloying, surface modification, surface coating, and agglomerating. It is further noted that in general the working step may be applied to solid hydrogen storage materials regardless of the form (i.e., ribbons, flakes, chunks, particles, etc) and regardless of how the solid hydrogen storage materials are formed. While it is preferably that the solid alloy is formed via a rapid solidification process, it is also possible that the solid alloy is formed by other means, such as by mechanically alloying, etc. Hence, in general, any solid hydrogen absorbing alloy, in any solid form, may be a precursor material to the working step of the present invention.

After a hydrided hydrogen storage alloy powder is formed, it may be loaded onto an electrode belt or substrate material for the purpose of making individual hydrogen absorbing alloy electrodes. An example of continuous fabrication process for electrodes starting from a comminuted hydrogen storage alloy powder is provided in U.S. Patent Application Number 4,915,898, the disclosure of which is incorporated by reference herein. In the present invention, it is preferred that the hydrogen storage alloy powder is deposited onto the belt as a metal hydride rather than as the corresponding metal. As noted above, the metal hydride is more stable and less flammable than the metal. After the hydrided material is loaded onto the belt, it may be compacting into the belt by a compacting device, such as by one or more rolling mills.

The present invention includes a metal hydride hydrogen storage means for storing hydrogen within a container or tank. In one embodiment of the present invention, the storage means comprises the aforementioned hydrogen storage alloy material physically bonded to a support means. Generally, the support means can take the form of any structure that can hold the storage alloy material. Examples of support means include, but are not limited to, mesh, grid,

matte, foil, foam and plate. Each may exist as either a metal or non-metal.

The support means may be formed from a variety of materials with the appropriate thermodynamic characteristics that can provide the necessary heat transfer mechanism. These include both metals and non-metals. Preferable  
5 metals include those from the group consisting of Ni, Al, Cu, Fe and mixtures or alloys thereof. Examples of support means that can be formed from metals include wire mesh, expanded metal and foamed metal.

The hydrogen storage alloy material may be physically bonded to the support means by compaction and/or sintering processes. The alloy material is  
10 first converted into a fine powder. The powder is then compacted onto the support means. The compaction process causes the powder to adhere to and become an integral part of the support means. After compaction, the support means that has been impregnated with alloy powder is preheated and then sintered. The preheating process liberates excess moisture and discourages  
15 oxidation of the alloy powder. Sintering is carried out in a high temperature, substantially inert atmosphere containing hydrogen. The temperature is sufficiently high to promote particle-to-particle bonding of the alloy material as well as the bonding of the alloy material to the support means.

The support means/alloy material can be packaged within the  
20 container/tank in many different configurations. Figure 9 shows a configuration where the support means/alloy material is spirally wound into a coil. Figure 10 shows an alternate configuration where the support means/alloy material is assembled in the container as a plurality of stacked disks. Other configurations are also possible (e.g. stacked plates).

25 Compacting and sintering alloy material onto a support means increases the packing density of the alloy material, thereby improving the thermodynamic and kinetic characteristics of the hydrogen storage system. The close contact between the support means and the alloy material improves the efficiency of the heat transfer into and out of the hydrogen storage alloy material as hydrogen is  
30 absorbed and desorbed. In addition, the uniform distribution of the support means throughout the interior of the container provides for an even temperature and heat distribution throughout the bed of alloy material. This results in a more

uniform rates of hydrogen absorption and desorption throughout the entirety thereof, thus creating a more efficient energy storage system.

One problem when using just alloy powder (without a support means) in hydrogen storage beds is that of self-compaction due to particle size reduction. That is, during repeated hydriding and dehydriding cycles, the alloy materials expand and contract as they absorb and desorb hydrogen. Some alloy materials have been found to expand and contract by as much as 25% in volume as a result of hydrogen introduction into and release from the material lattice. As a result of the dimensional change in the alloy materials, they crack, undergo fracturing and break up into finer and finer particles. After repeated cycling, the fine particles self-compact causing inefficient hydrogen transfer as well as high stresses that are directed against the walls of the storage container.

However, the processes used to attach the alloy material onto the support means keeps the alloy particles firmly bonded to each other as well as to the support means during the absorption and desorption cycling. Furthermore, the tight packaging of the support means within the container serves as a mechanical support that keeps the alloy particles in place during the expansion, contraction and fracturing of the material.

The instant alloys and storage material systems are useful as hydrogen supplies for many applications. One such application is the field of automobiles. Specifically, the systems can be used as a source of hydrogen for internal combustion engine (ICE) vehicles or fuel cell (FC) vehicles.

Figure 11 shows a schematic representation of a hydrogen gas supply system for an ICE vehicle, which is for supplying a hydrogen engine 1 with hydrogen gas. The system has a hydrogen gas storage portion 2 and an engine waste heat transfer supply passage 3 which leads engine waste heat (in the form of exhaust gas or engine coolant) discharged from the engine 1 to the hydrogen gas storage portion 2. The system also includes a return passage 4 for returning any engine coolant used to heat the hydrogen storage material back to the engine 1 and an exhaust gas vent 7 for releasing used exhaust gas. The system further includes a hydrogen gas supply passage 5 which leads hydrogen gas from the hydrogen gas storage portion 2 to the engine 1. The engine waste heat

transfer supply passage 3 is provided with a temperature regulating portion 6 which regulates the temperature of the waste heat to be introduced into the hydrogen gas storage portion 2. With such a system, waste heat generated within the ICE can be efficiently used to heat the hydrogen storage material to release hydrogen therefrom for use in the ICE.

Figure 12 shows a schematic representation of a hydrogen gas supply system for an FC vehicle, which is for supplying a fuel cell 8 with hydrogen gas. The system has a hydrogen gas storage portion 12 and a fuel cell waste heat/hydrogen transfer supply passage 9 which leads fuel cell waste heat and unused hydrogen discharged from the fuel cell 8 to a hydrogen gas combustor 10. Waste heat from the fuel cell may be in the form of heated gases or heated aqueous electrolyte. The hydrogen combustor 10, heats a thermal transfer medium (preferably in the form of the aqueous electrolyte from the fuel cell) utilizing waste heat from the fuel cell 8, and by combusting hydrogen. Hydrogen is supplied to the combustor 10 via unused hydrogen from the fuel cell 8, and via fresh hydrogen supplied from the hydrogen storage unit 12 via hydrogen supply line 14. Heated thermal transfer medium is supplied to the hydrogen storage unit 12 via supply line 13. The system also includes a return passage 16 for returning any fuel cell aqueous electrolyte used to heat the hydrogen storage material back to the fuel cell 8 and an exhaust gas vent 15 for releasing used combustor gas. The system further includes a hydrogen gas supply passage 11 which leads hydrogen gas from the hydrogen gas storage unit 12 to the fuel cell 8.

While the invention has been described in connection with preferred embodiments and procedures, it is to be understood that it is not intended to limit the invention to the described embodiments and procedures. On the contrary it is intended to cover all alternatives, modifications and equivalence which may be included within the spirit and scope of the invention as defined by the claims appended hereinafter.

We claim:

1. A method for making a hydrogen storage material, said method comprising the steps of:

providing a solid precursor hydrogen storage material; and

working said precursor material in a hydrogen atmosphere at conditions sufficient to hydride said material.

2. The method of claim 1, wherein said providing step comprises the steps of: providing component materials;

melting said component materials together to form a molten material; and rapidly solidifying said molten material to form said solid precursor material.

3. The method of claim 2, wherein said rapidly solidifying step is accomplished using melt spinning.

4. The method of claim 2, wherein said solidifying step is accomplished using gas atomization.

5. The method of claim 1, wherein said working step comminutes said solid material into a powder.

6. The method of claim 1, wherein said working step mechanically alloys said solid material.

7. The method of claim 1, wherein said working step mechanically alloys said material with a least one additional material.

8. The method of claim 1, wherein said working step modifies the surface of said solid material.

9. The method of claim 1, wherein said working step coats the surface of said

solid material with at least one additional material.

10. The method of claim 1, wherein said conditions include a hydrogen pressure between about 10 bar and about 100 bar.

5

11. The method of claim 1, wherein said conditions include a hydrogen pressure between about 20 bar and about 60 bar.

10

12. The method of claim 5, wherein said method further comprises the step of: loading said hydrided alloy powder onto an electrode belt.

13. The method of claim 5, wherein said powder has a particle size less than 70 microns.

15

14. The method of claim 5, wherein said powder has a particle size less than 50 microns.

15. The method of claim 5, wherein said powder has a particle size less between about 30 microns and about 70 microns.

20

16. The method of claim 1, wherein said worked material comprises at least one element selected from the group consisting of magnesium, and nickel.

25

17. The method of claim 1, wherein said worked material has a hydrogen storage capacity of at least 6 weight %,.

18. The method of claim 1, wherein said worked material has an absorption kinetics of 80% capacity within 5 minutes at 300 °C.

30

18. The method of claim 1, wherein said worked material includes at least 90 weight % magnesium.

19. The method of claim 1, wherein said worked material is a alloy including 0.5-2.5 weight % nickel.

22. The method of claim 1, wherein said worked material is an alloy including 1.0-4.0 weight % Misch metal.

23. The method of claim 22, wherein said worked material is a Misch metal comprising Ce, La and Pr.

24. The method of claim 1, wherein said worked material is an alloy including at least one element from the group consisting of 3-7 weight % Al, 0.1-1.5 weight % Y, and 0.3-1.5 weight % silicon.

25. The method of claim 1, wherein said worked material is an alloy comprising 91.0 wt.% Mg, 0.9 wt.% Ni, 5.6 wt.% Al, 0.5 wt.% Y and 2.0 at% Misch metal.

26. The method of claim 1, wherein said worked material is an alloy comprising 95 wt.% Mg, 2 wt.% Ni and 3.0 wt% Misch metal.

27. The method of claim 1, wherein said working step is performed in an attritor.

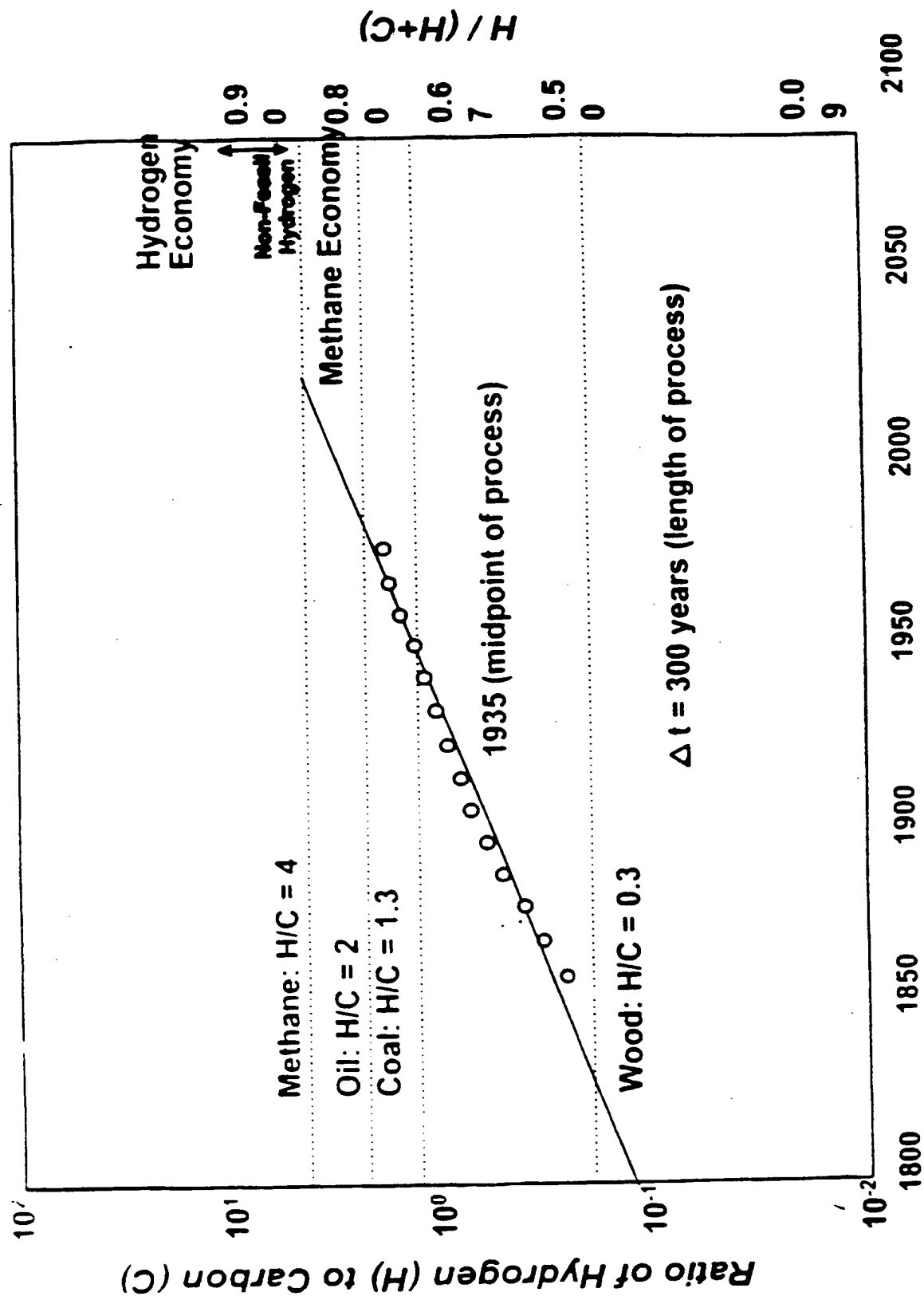
28. The method of claim 1, wherein said working step comprises an attriting step.



1 / 11

Figure 1

## Underlying Decarbonisation



# *Absorption Kinetics*

- Surface Catalytic Activity

- Catalytic sites

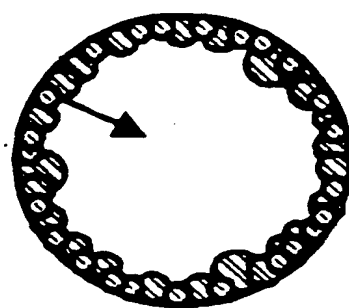
- Surface area

- Nucleation Density

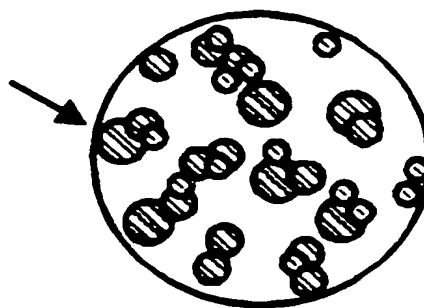
- Surface nucleation

- Bulk nucleation

- Growth Rate

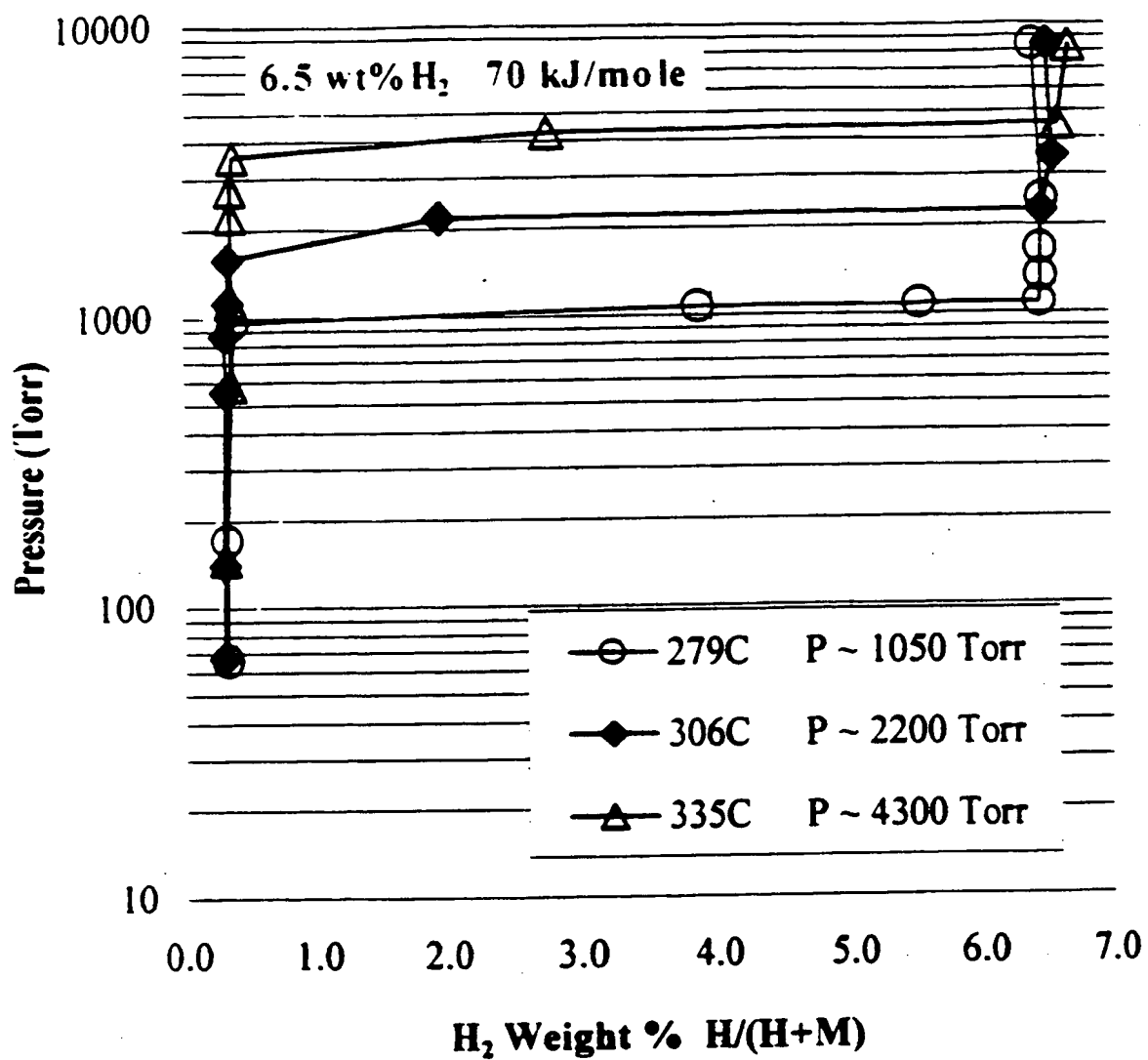


Surface Nucleation



Bulk Nucleation

Figure 2

**Figure 3**

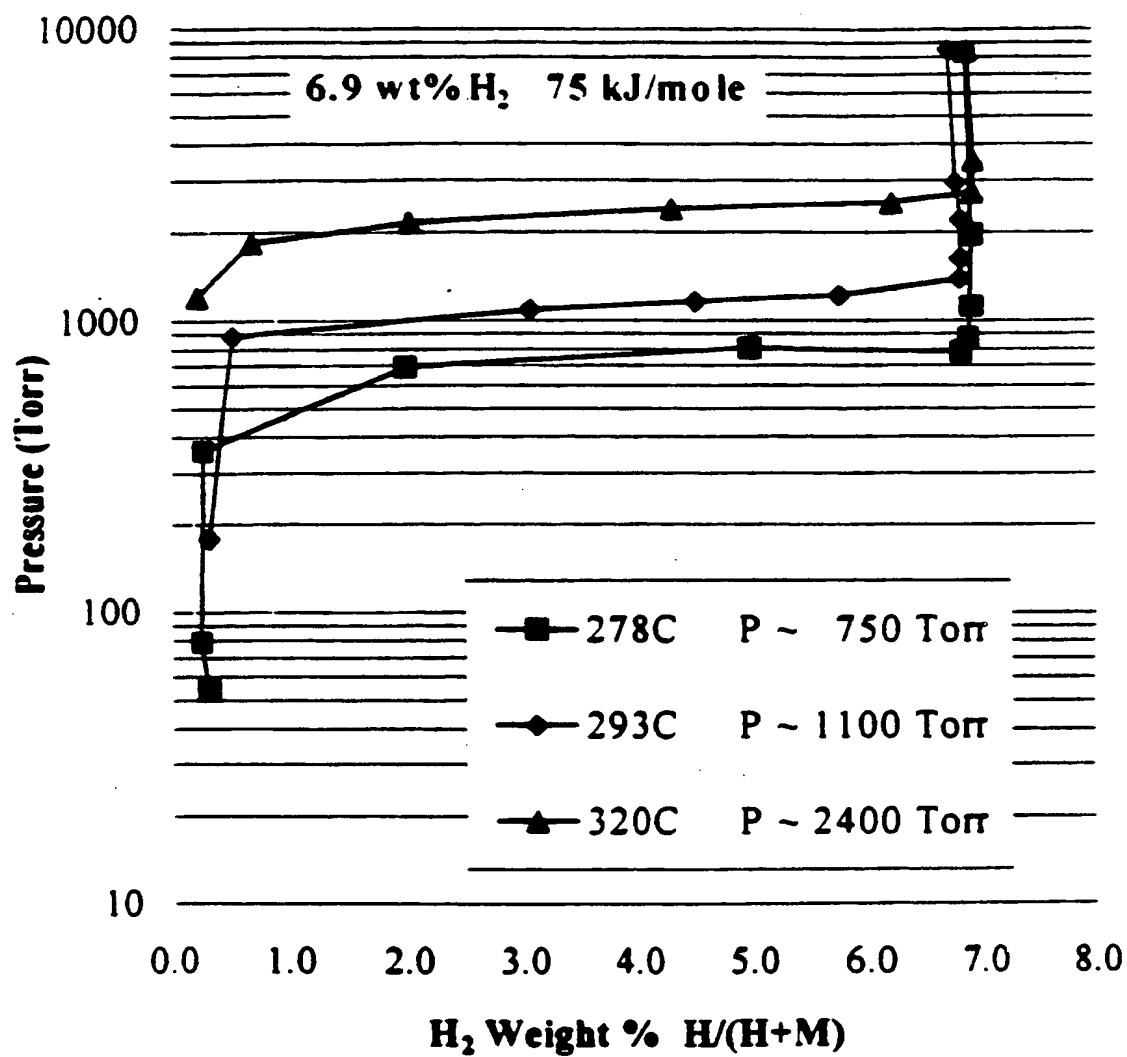


Figure 4

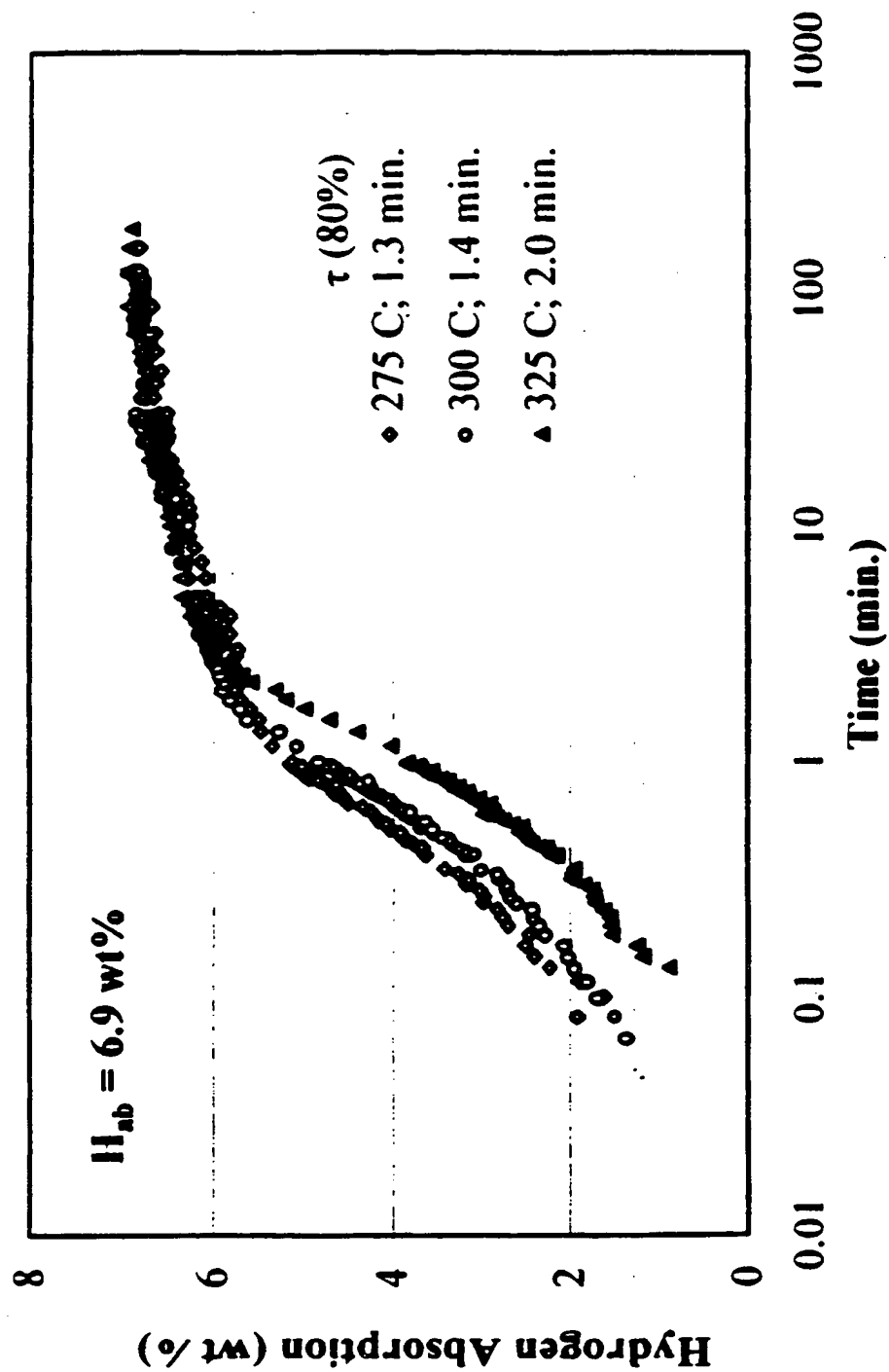


Figure 5

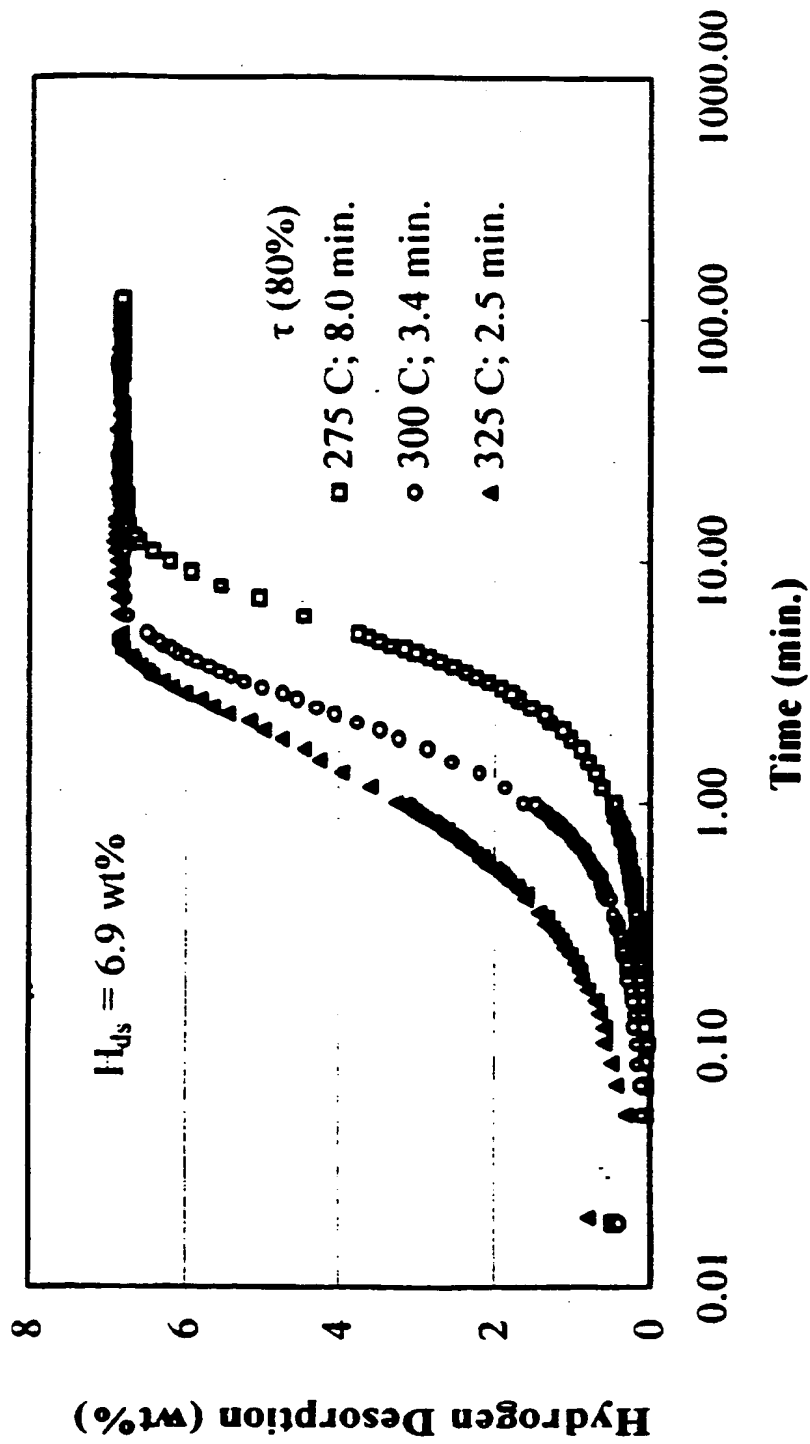


Figure 6

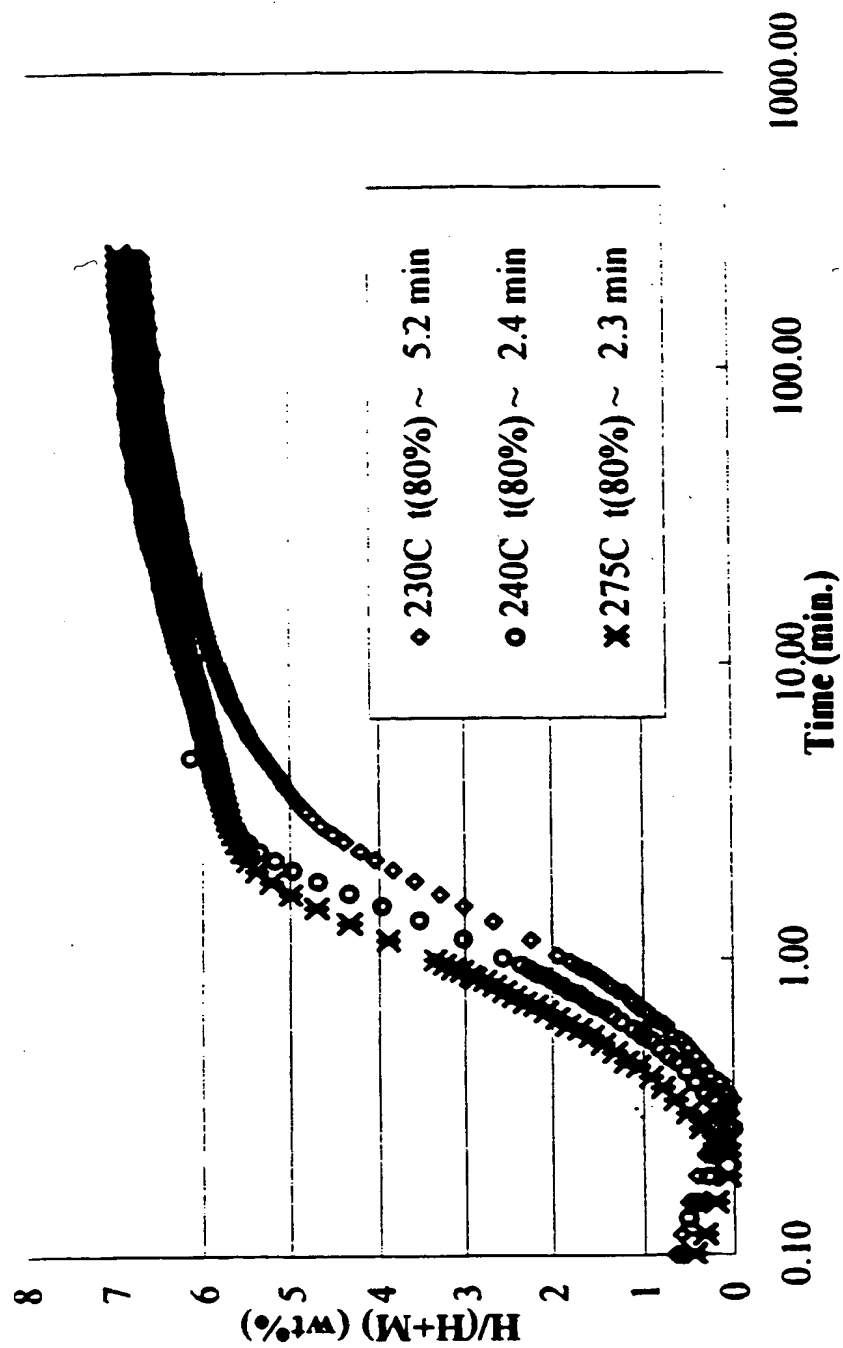


Figure 7

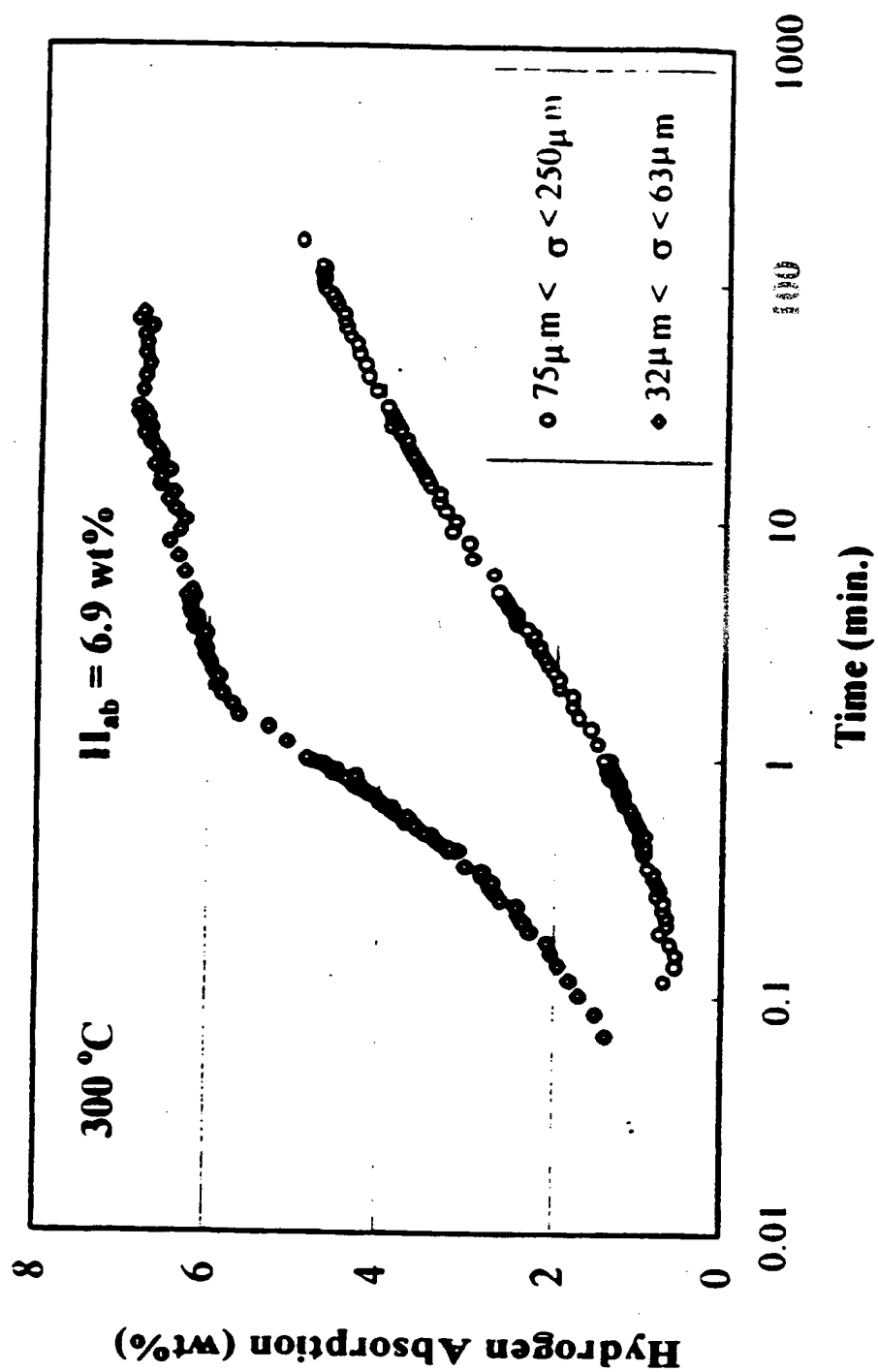


Figure 8



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(54) Title: METHOD FOR MAKING HYDROGEN STORAGE ALLOY

(57) Abstract: A method for making a hydrided hydrogen storage alloy powder from component material. In the present method a material is worked at the same time it is hydrided. Working preferably involves comminution of the material.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US00/32871

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(7) : C22C 23/00, 23/02

US CL : 148/538, 549, 552, 555, 556, 561, 666, 667, 675, 676; 252/188.25, 188.26; 420/402, 405, 407, 441, 528, 542, 546, 578, 900; 423/644, 645, 647; 429/218, 223

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : Please See Continuation Sheet

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X, E --- Y, E	US 6,174,345 B1 (CHEN et al.) 16 January 2001 (16.01.2001), column 3, line 57-column 4, line 9; column 6, lines 49-52.	1-2, 4-5, 8-10, 13-14, 16 ----- 3, 12
X --- Y	US 5,916,381 A (SAPRU et al.) 29 June 1999 (29.06.1999), column 6, line 63-column 7, line 18; column 8, lines 13-31; column 10, lines 39-48	1, 6-9, 16, 18, 26-27 ----- 2, 12, 19
Y, E	US 6,193,929 B1 (OVSHINSKY et al.) 27 February 2001 (27.02.2001), column 8, lines 49-67; column 10, lines 27-65; column 11, lines 24-33; column 12, lines 35-40.	3-5, 7-9, 12-27
A	US 4,431,561 A (OVSHINSKY et al.) 14 February 1984 (14.02.1984).	1-27
A	US 5,840,440 A (OVSHINSKY et al.) 24 November 1998 (24.11.1998).	1-27
A,E	US 6,210,498 B1 (OVSHINSKY et al.) 03 April 2001 (03.04.2001).	1-27

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

\* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&amp;" document member of the same patent family

Date of the actual completion of the international search

25 May 2001 (25.05.2001)

Date of filing of the international search report

15 JUN 2001

Name and mailing address of the ISA/US

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# INTERNATIONAL SEARCH REPORT

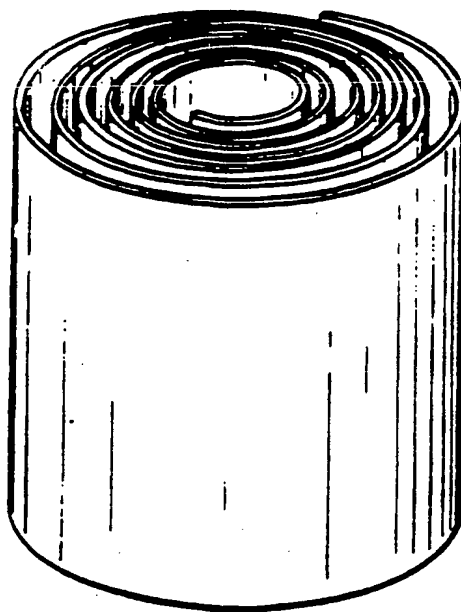
International application No.

PCT/US00/32871

**C ntinuation of B. FIELDS SEARCHED Item 1:** 148/538, 549, 552, 555, 556, 561, 666, 667, 675, 676; 252/188.25, 188.26; 420/402, 405, 407, 441, 528, 542, 546, 578, 900; 423/644, 645, 647; 429/218, 223

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**Figure 9**



**Figure 10**

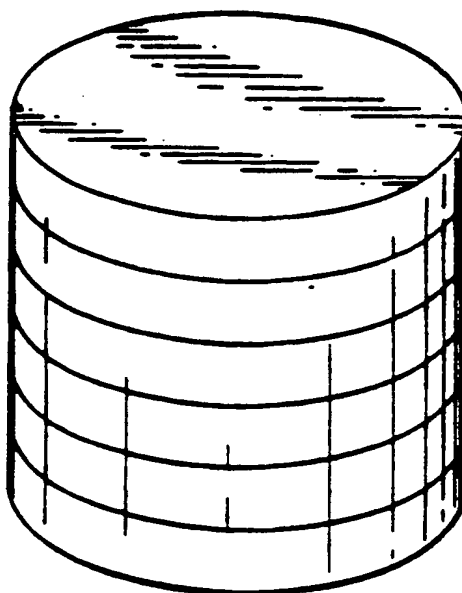


Figure 11

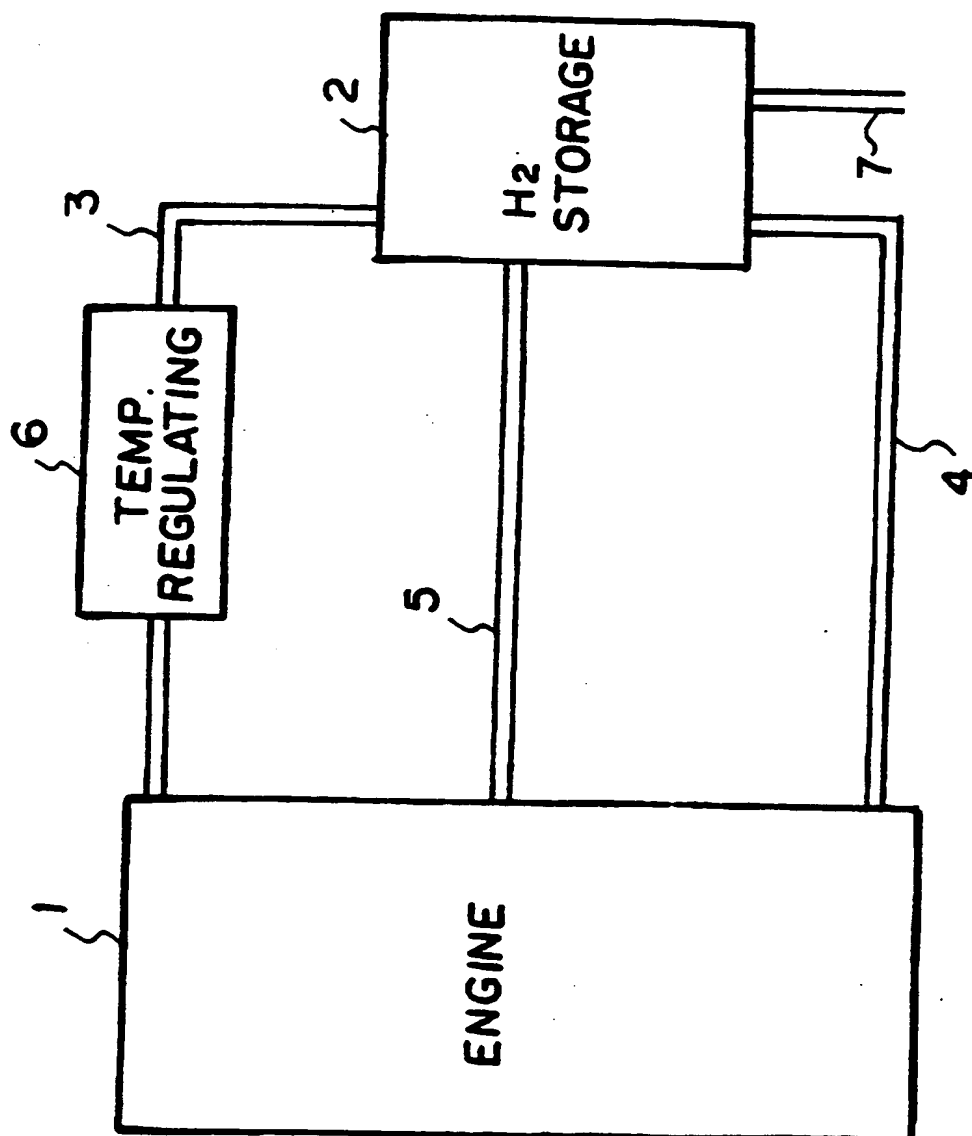
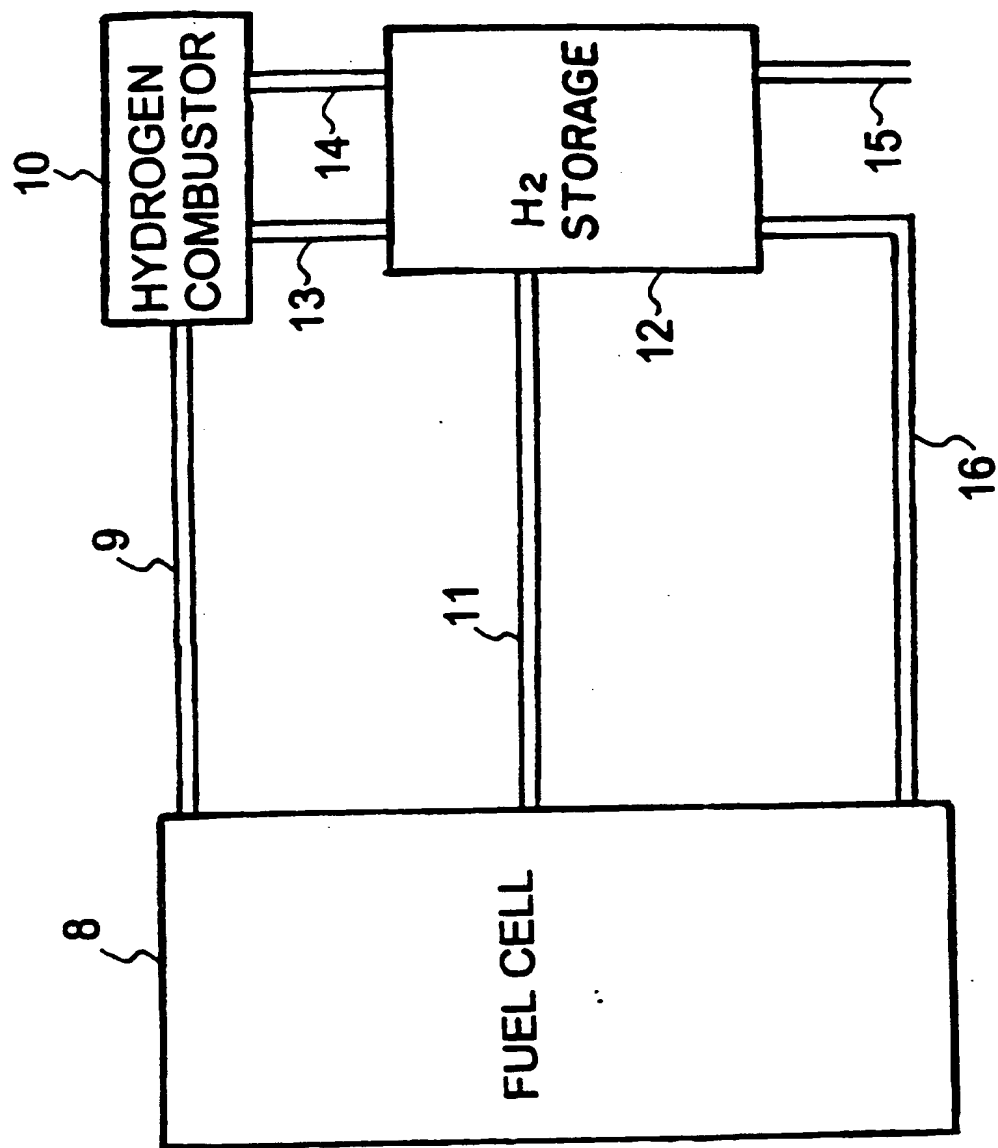


Figure 12



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